ALUMINUM EFFECT ON THE CALIBRATION OF THE EU OXYBAROMETER FOR NAKHLITES. J. Makishima[1], G. McKay[2], L. Le[3], M. Miyamoto[1] and T. Mikouchi[1]. [1]Department of Earth and Planetary Science, Graduate school of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan, makki@eps.s.u-tokyo.ac.jp, [2]Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, USA, [3]ESC Group, Jacobs Sverdrup, Houston, TX 77058, USA.

Introduction: Recent studies of Martian meteorites have shown that Martian magma had wide range of oxygen fugacity. In order to estimate the redox state of the Martian crust and mantle, the partitioning coefficient of Eu in the shergottite pyroxene has been extensively studied [1-3]. Nakhlite, a cumulate clinopyroxenite, is another important group of Martian meteorites. We have studied synthetic compositions (NT, NL, NJ, NJ2 and NJ4) in order to estimate the Nakhla parent melt composition [4,5]. In our previous work [6], we calibrated the Eu oxybarometer for nakhlite using the NJ4 composition which we believe is the closest to the Nakhla parent melt. Consequently, we concluded that Nakhla may have crystallized under fairly reducing condition (Table1, Fig.1). However, we also found that the partition coefficient is strongly affected by Al contents in melt and in pyroxene [7]. In this abstract we report the correlation between the D values and Al contents in melt and in pyroxene from our Nakhla experimental studies. Also we check the reliability of our previous calibration of Eu oxybarometer, because REEs are easily affected by Al content in melt and in pyroxene and Nakhla pyroxene shows unusual patchy Al zoning.

Table. 1		Pyroxene D(Eu)/D(Gd)	
Expt	**fO2**	**D(experiment)**	**D(Nakhla)**
817	**IW**	**0.64±.002**	**0.7±0.1**
818	**IW+1.5**	**0.76±0.02**	
819	**QFM**	**0.86±0.04**	
Oe [8]	**QFM**	**0.86±0.03**	

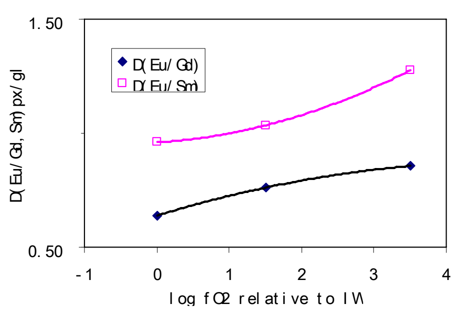

Fig. 1 Calibration of D(Eu/Gd)(pyroxene/glass) and D(Eu/Sm) (pyroxene/glass) versus oxygen fugacities (in log units relative to the IW buffer).

Experimental method: We doped the NJ4 composition with ~1 wt% Sr and REEs, which is a starting material. Then, we put it in the furnace at 1300 ºC for 48 hours to homogenize it, quenched and put back below the liquidus under the three oxygen fugacities, IW, IW+1.5 and QFM (IW+3.5), growing pyroxene. Table 2 summarizes thermal histories of these runs. We analyzed samples with the Cameca SX-100 Electron Microprobe at JSC and calculated the D(Eu/Gd).

	Table 2. Cooling histories for experiments			
Expt.	**Oxygen fugacity**	**Start cooling**	**Quench temperature**	**Cooling rate**
817	**IW**	**1155ºC**	**1150ºC**	**0.5ºC/h**
818	**IW+1.5**	**1155ºC**	**1150ºC**	**0.5ºC/h**
819	**QFM**	**1159ºC**	**1152ºC**	**0.5ºC/h**

Results and Discussion: The effects which Al has on D values of REEs are complex. D values are affected not only by Al contents in melt but also by Al contents in pyroxene. Oe et. al. [7,8] grew pyroxene from the various synthetic compositions similar to Nakhla and studied the correlation between D(Ce), one of the trivalent REEs, and Al_2O_3 content in melt for each composition. As is clearly shown in Fig. 2, there is a positive correlation between D(Ce) and Al_2O_3 in melt.

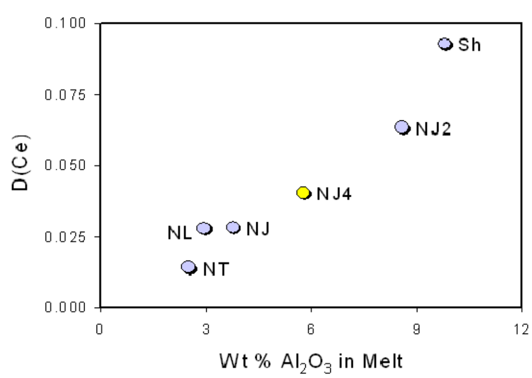

Fig. 2 D(Ce, pyroxene/melt) vs. Al_2O_3 content in pyroxene for experimental pyroxene compositions. NJ4, NL, NT, NJ and NJ2 are synthetic compositions similar to Nakhla and Sh is similar to Shergotty [7].

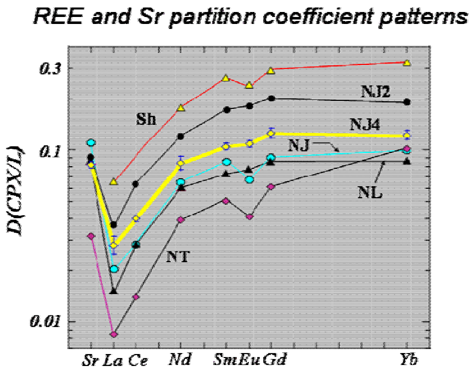

Fig. 3 The partition coefficient patterns for REEs of synthetic compositions [7].

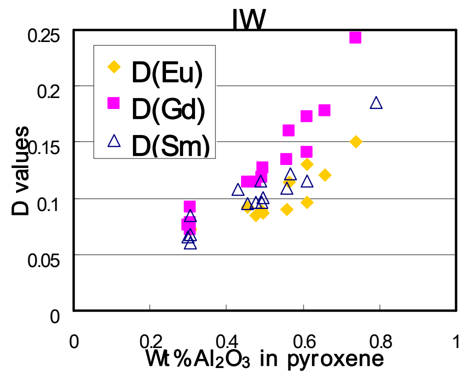

Fig. 4 D values vs. Al_2O_3 in pyroxene at the IW buffer.

D values of other REE also have similar correlation with Al content in melt (Fig. 3). There is almost an order of magnitude variation in partition coefficients over a range of synthetic Nakhla compositions.

Moreover, Fig. 4 shows that Al contents in our NJ4 synthetic pyroxene at the IW buffer also have strong effects on D values of REEs. Similarly we found Al contents in pyroxene and D values have positive correlation at the IW+1.5 and QFM.

As is shown in the Figs. 5 and 6, D(Sr) and the square root of D(Sm)*D(Gd) are almost the same both at the IW and QFM. This means that our Eu oxybarometer for nakhlite in the previous study may not work for the NJ4 composition. The reason for this is as follows. Under mantle-like condition only Eu among REEs exists in bivalent state and trivalent state, respectively under more reducing condition and more oxidizing condition. Eu behaves differently from the other REEs and we expect a deeper Eu anomaly in the more reducing condition. Eu^{2+} behaves similarly to Sr and Eu^{3+} behaves like intermediate element between Sm and Gd. Therefore, when D(Sr) and the square root of D(Sm)*D(Gd) are almost the same, the there is little difference between D(Eu^{2+}) and D(Eu^{3+}). In this case the Eu anomaly will be very small for the NJ4 composition. Because Sr is difficult to analyze with the electron microprobe, we need more accurate analyses of D(Sr) with the ion microprobe to confirm this observation.

Consequently, it is difficult to know the accurate D values of REEs in nakhlite because they are affected in a complex way by Al contents both in melt and in pyroxene. Thus, we must be careful to use the appropriate partition coefficient values when we perform SIMS analyses of nakhlite pyroxene and estimate the melt composition with partition coefficients.

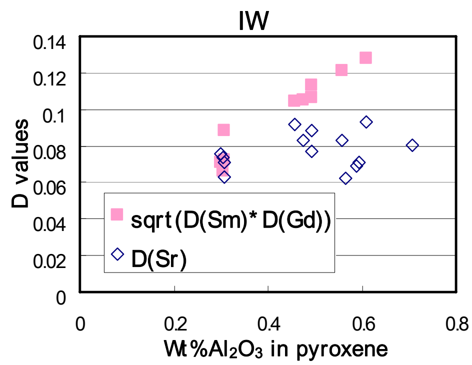

Fig.5 D values vs. Wt% Al_2O_3 in pyroxene at the IW

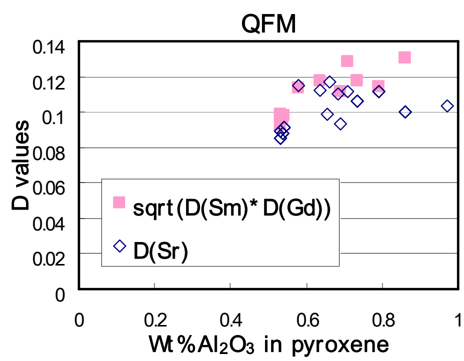

Fig. 6 D values vs. Wt% Al_2O_3 in pyroxene at the QFM

References: [1] Wadhwa M. (2001) *Science*, *291*, 1527-1530. [2] McCanta M. et al. (2004) *GCA*, *68*, 1943-1952. [3] Wadhwa M. et al. (1994) *GCA*, *58*, 4213-4229. [4] McKay G. et al. (1994) *LPSXXV*, 883-884. [5] Kaneda K. et al. (1998) *LPSXXIX*, 1620-1621. [6] Makishima J. et.al. (2006) *LPSXXXVII*, #1589. [7] Oe K. et al. (2001) *LPS XXXII*, #2174. [8] Oe K. et al. (2002) *LPS XXXIII*, #2065.